In Situ Chemical Oxidation of VOCs and BTEX Plume in Low-Permeability Soils

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Process Map

Maintenance Yard

- Diesel, gasoline, solvents

Client Goals

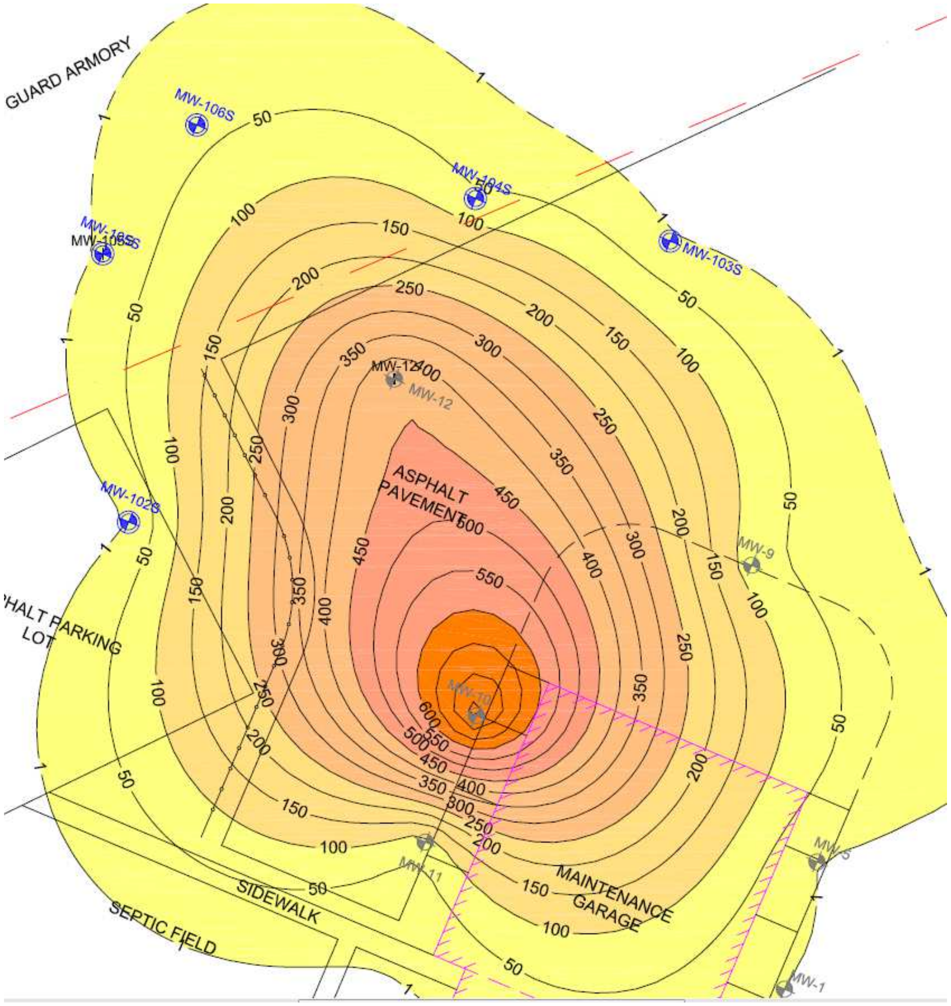
- Attain NJ GWQS - Rapidly

Challenges

- Mixed plume in low perm soil

Evolution of CSM

- Benefits of real time CSM evolution



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Process Map

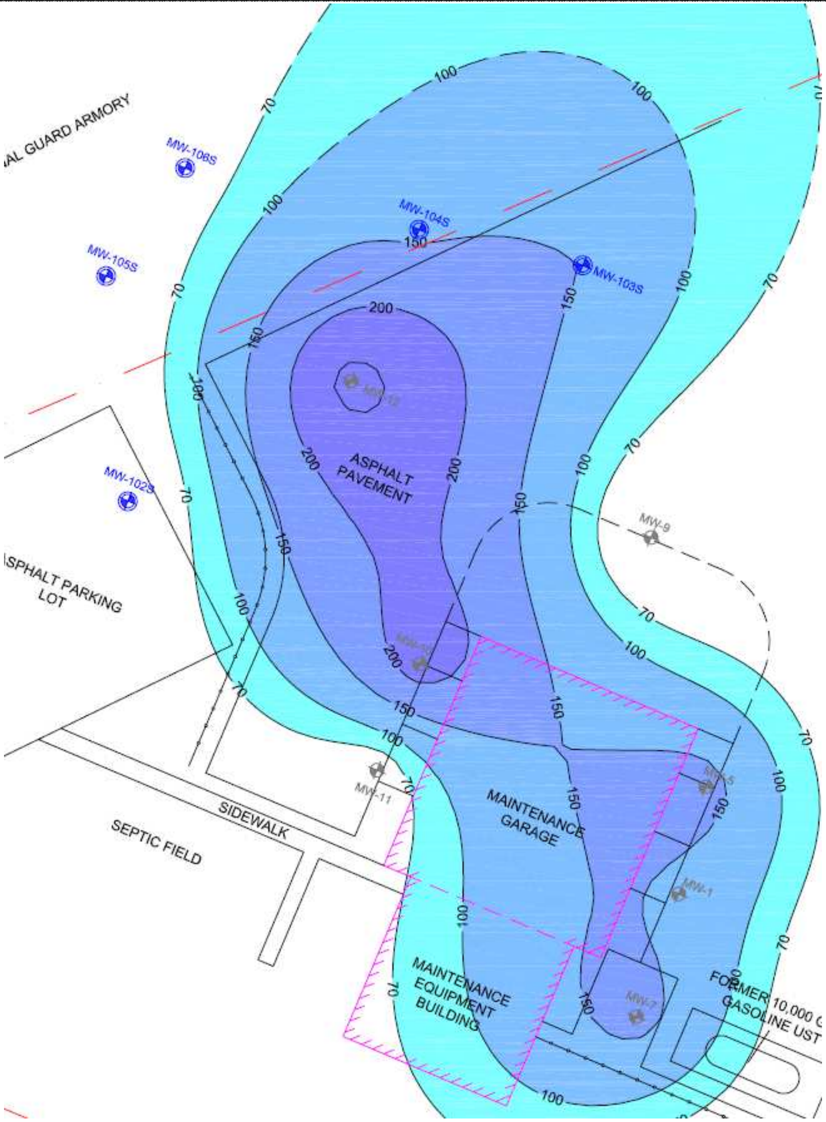
Thoughts on Data Interpretation

- Low perm soils & MIP results

Evolution of Remedial Approach

- Alternate oxidants

Results & Path Forward



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Site History

1998

- 4,000g Diesel UST
- 2,000g Diesel UST

2001

- 10,000g Gas UST
- VOC Storage Bldg
- Fuel dispenser

2002 -2005

- Wells Installed
- BTEX; MTBE; TBA
- Lead
- TCE; cis-1,2-DCE; VC
- 1,2-DCA; 1,1-DCE

2007 - 2008

- Previous COCs
- PCE

Initial Conceptual Site Model – Hydrogeology

Asphalt

0.5 ft

Brown to grey Silt + med to fine sand, trace clay

2 ft, occasionally

10 ft

Dark grey clayey Silt

90 ft

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Remedial Notions - Based on 2008 CSM

CHP as remedial approach

- Site geochemistry preferable for CHP
  - High dissolved iron content
  - Site pH is low (4-6) range
- Iron a catalyst for hydroxyl radical generation
- Acidic pH assists keeping iron in solution & available for reaction
- Site contaminants susceptible to immediate oxidation by CHP
- Cons: potential TBA (as by-product MTBE oxidation) generation

Plus, added benefits :

- Oxygen generated by hydrogen peroxide decomposition aids aerobic biological systems
- Site contaminants (TBA, MTBE, benzene, and VC) susceptible to long-term aerobic biological degradation

Remedial Focus

2009

EXTERNAL BENCH STUDY

- One saturated (8 – 13 ft bgs) soil sample
- Groundwater
- Sample from or adjacent to well with highest concentration (MW-10 @ MIP-6 and MIP-7)
- Acidic buffer capacity / Peroxide reactivity / Oxidant effectiveness

BENCH RESULTS

- Initial VOCs: gw 1.5 mg/L VOCs; soil 0.404 mg/kg
- Soil pH <4 to start
- Native iron deemed insufficient; iron addition recommended
- For all dose ratios: Target COCs degraded in soil & gw
- For all dose ratios: acetone accumulated; TBA accumulated or same

Recent History

2009

- Aug to Sep - Peroxide Injections

2010

- Nov – MIP / HPT
- Revise CSM

2011

- SPS Injections

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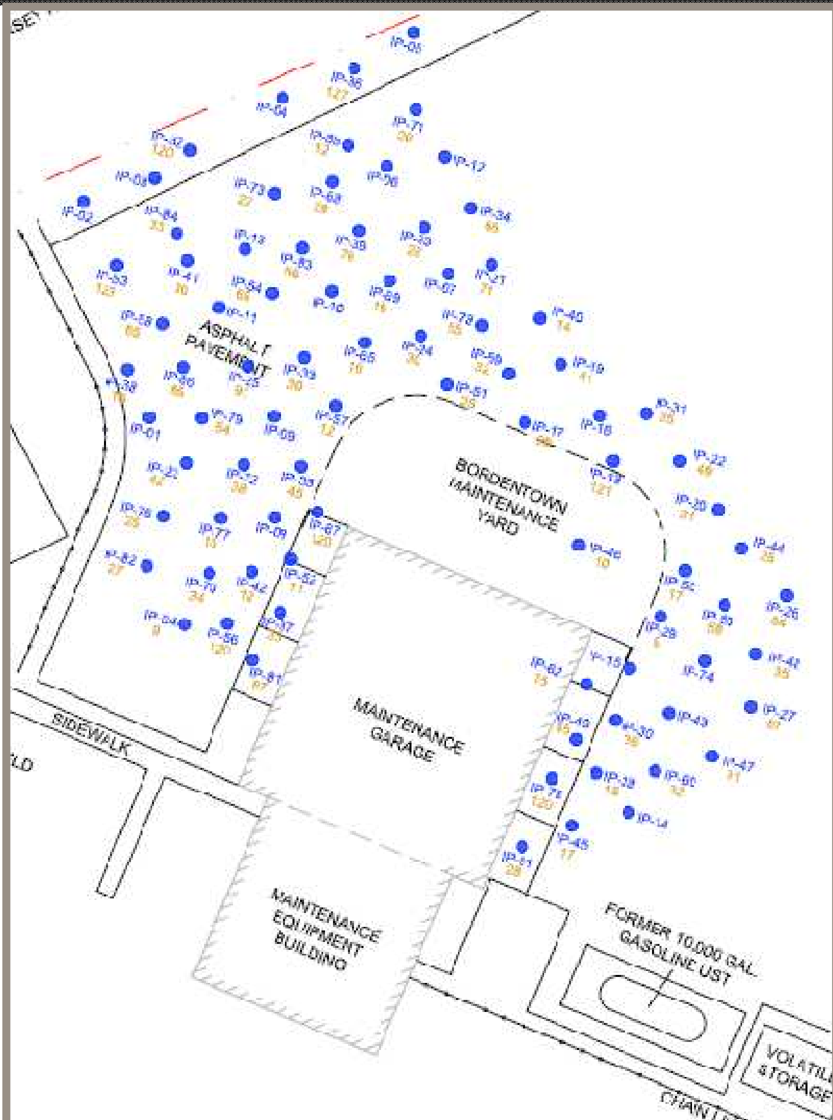
Phase I ISCO Application Summary



2009

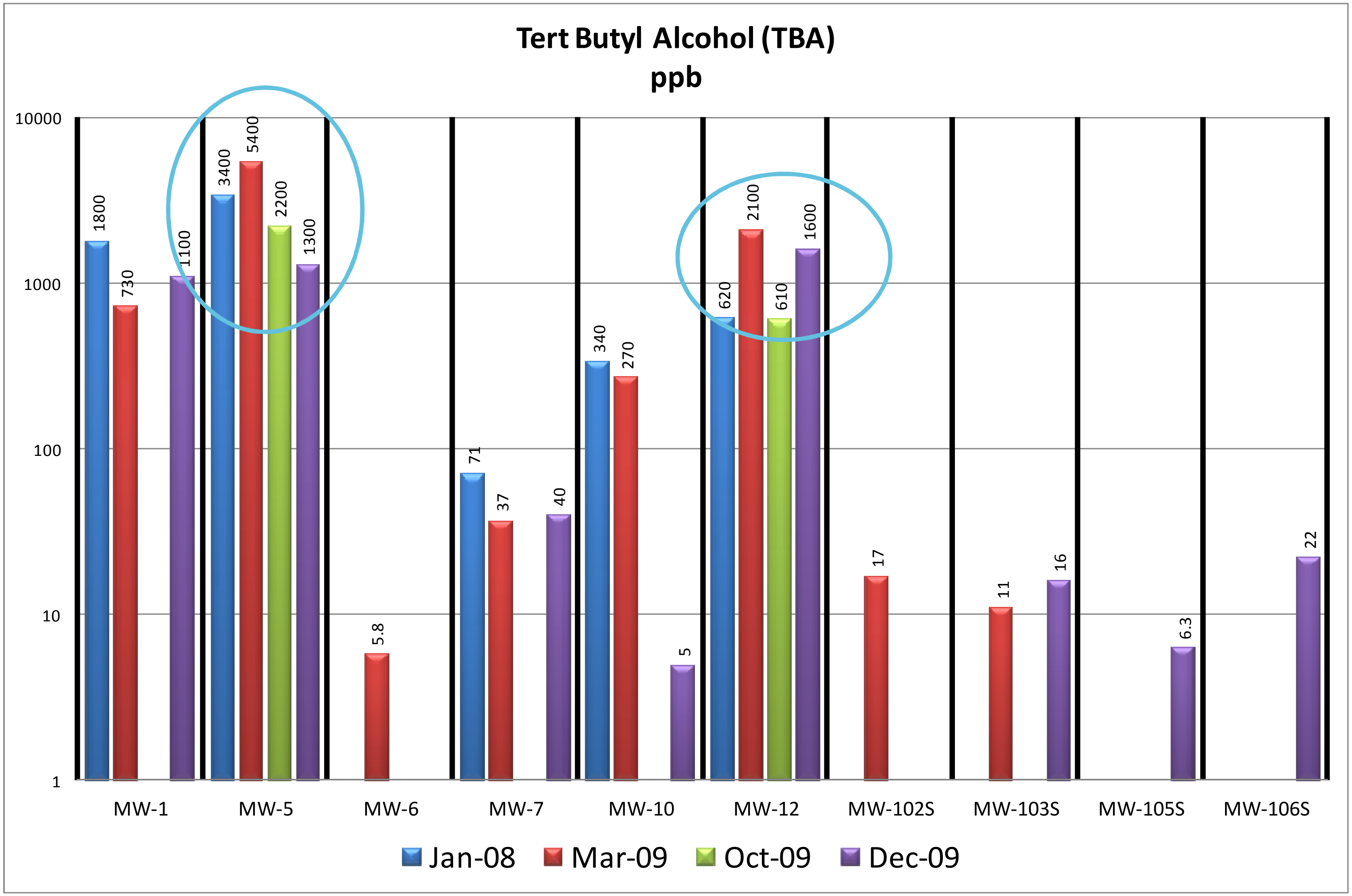
Round 1 – August 2009

- Could not inject target volume (500 gal of 14% H_2O_2) due to surfacing.
- Reduced H_2O_2 from 14% to 8% to 4%.
- Eliminated addition of iron after IP-12.

Round 2 – September 2009

- Used Hydraulic Profile Tool (HPT) on day 1 to establish permeable zones to target injections.
- Completed injections (IP 17 - 78) but at reduced target volume (120 gallons).
- Overall, actual volume <<< target volume.

Phase I ISCO Results Summary



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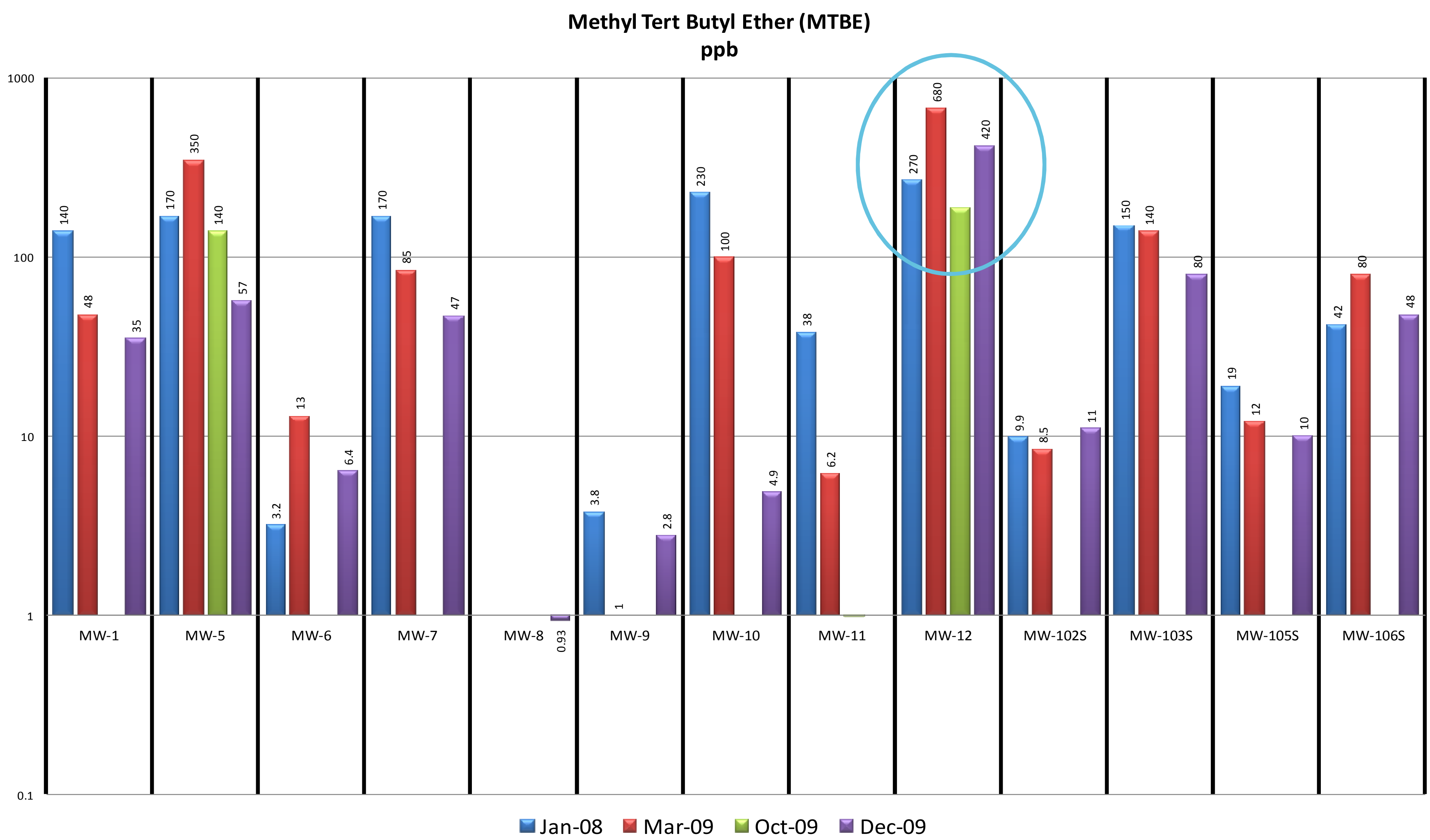
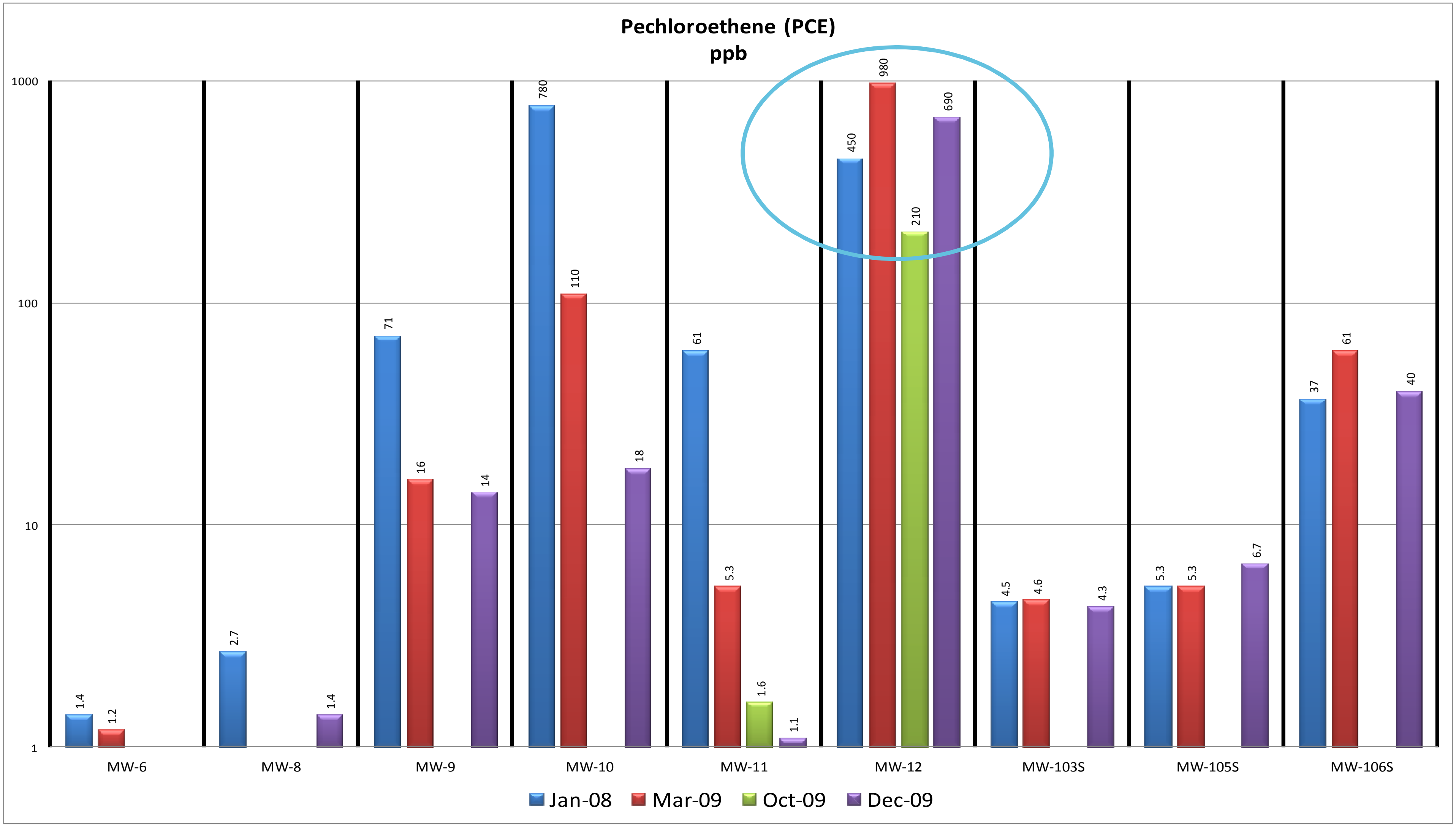
Phase I ISCO Results Summary



Phase I ISCO Results Summary



Phase I ISCO Lessons Learned

Injection volumes restricted

- Poor performance > 7ft bgs.

HPT data clarifies delivery issues.

- Injections forced to target 5 to 7 feet depth interval.

Rapid reaction of Catalytic Hydrogen Peroxide evolves gas = back pressure.

- Back pressure reduces ability to inject further oxidant solution.
- Difficult to inject volumes into areas previously injected.

Follow up treatment of residual “hot spots” warranted.

- Rebound / back diffusion?
- Permanent injection wells?

Phase II

"Hot Spot" treatment

- Strategy focusing on greatest residual
- Use MIP/HPT direct sensing to focus "Hot Spot" treatment efforts
- Identify zones of flux

Apply **different** oxidant - SPS

- Strong oxidizing radical
- Catalyzed by native iron
- **No** temperature increase
- No off-gas
- Oxidation & reduced formation of TBA (suggested in lit.)
- More Persistent
- Lower affinity for natural soil organics (Brown 2003); greater efficiency

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MIP in Low Perm Soil

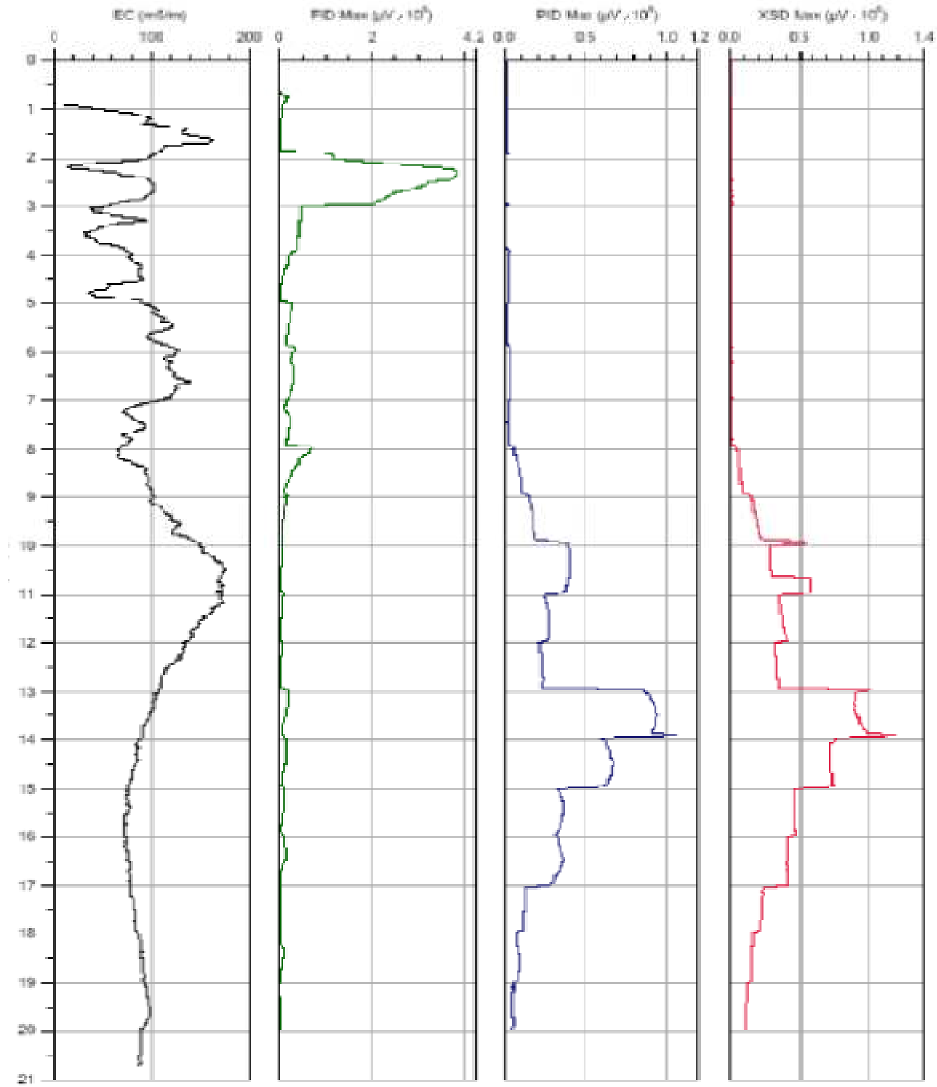
MIP Operator Observations

- PID readings >11 ft bgs suggestive of mg/L to 10s mg/L conc.?
- Signal in multiple areas of high soil conductivity

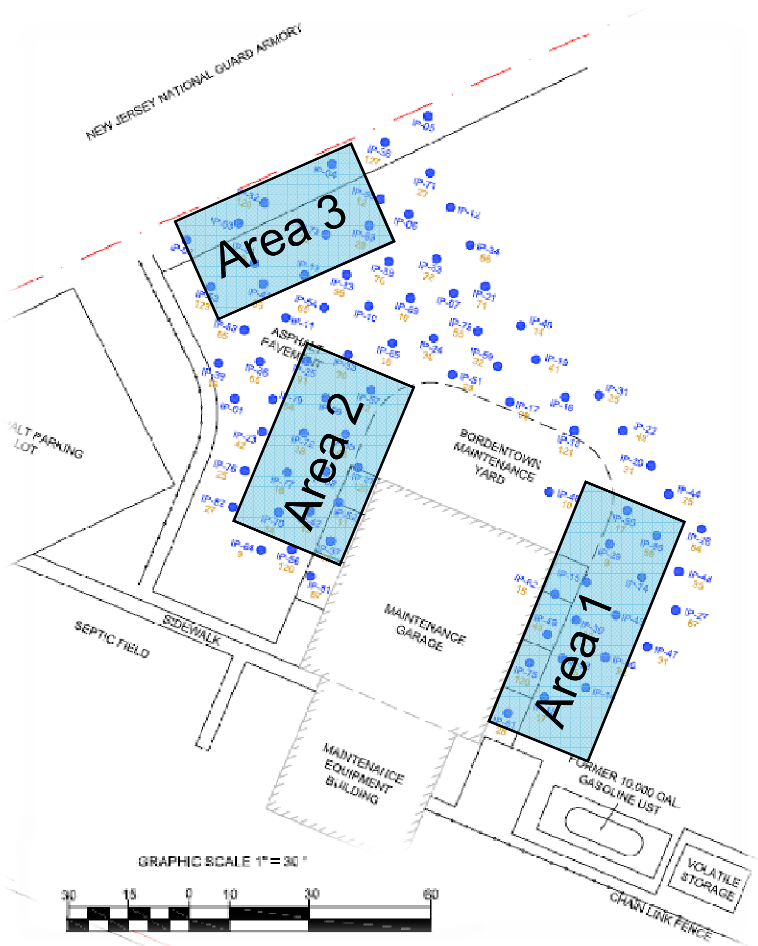
Multiple grab samples at depth do not confirm

Signal Bias in Low Perm Soil

- Others (*Quinnan, et al)* have documented bias in MIP within low permeability units
- + varying sensitivity depending on chlorine substitution



Phase II ISCO Application – January 2011



2011

Area 1

- 23 injection points
- Catalyst – 575-gallon
- 15% persulfate – 1,885-gallon
- Flow Rate – 1 gpm – 3.57 gpm

Area 2

- 42 injection points
- Catalyst – 1,710-gallon
- 15% persulfate – 5,925-gallon
- Flow Rate – 0.76 gpm – 3.85gpm

Area 3

- 24 injection points
- Catalyst – 600-gallon
- 15% persulfate – 2,200-gallon
- Flow Rate – 0.58 gpm – 2.78 gpm

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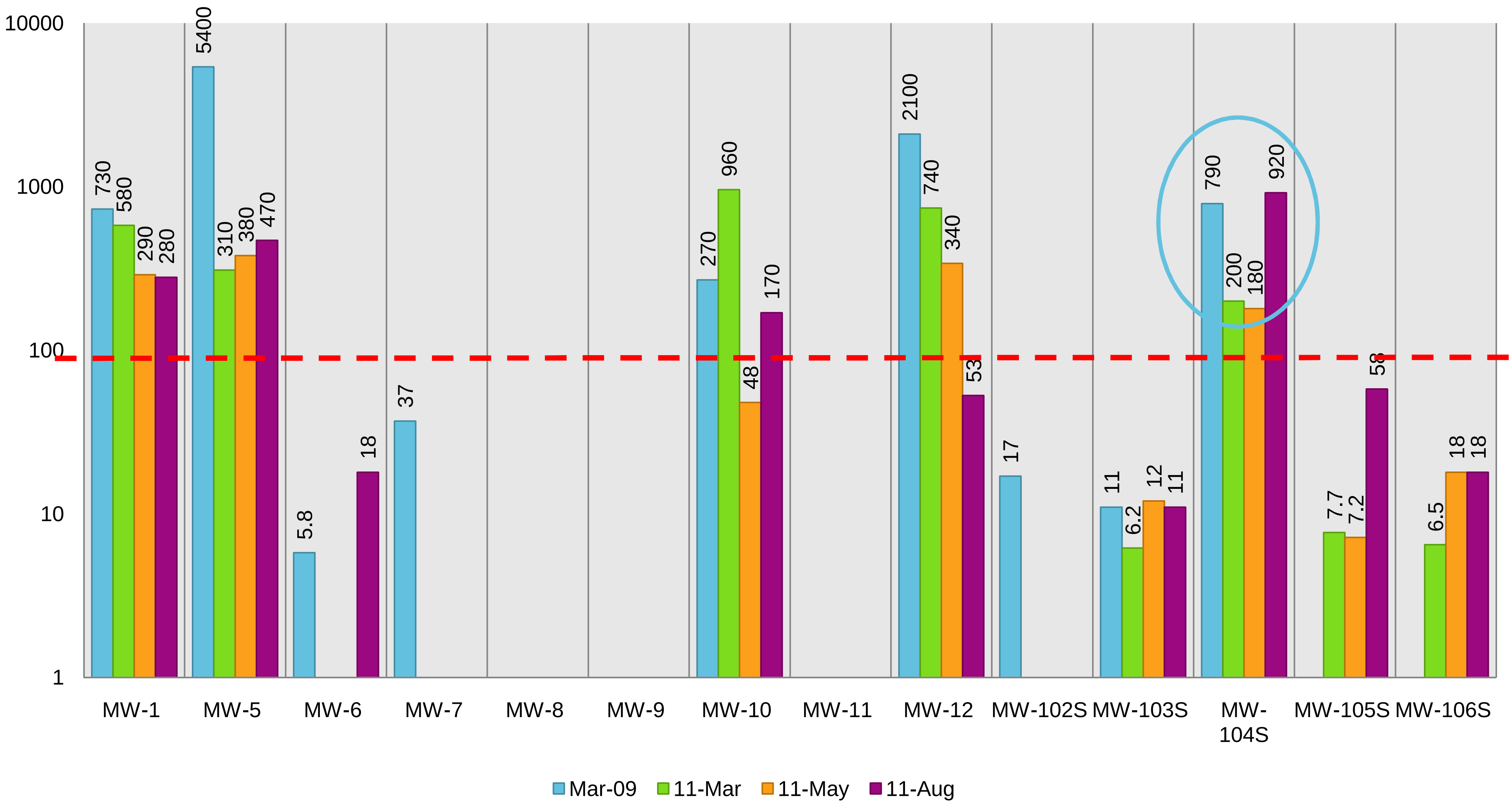
Phase II ISCO Results Summary - TBA



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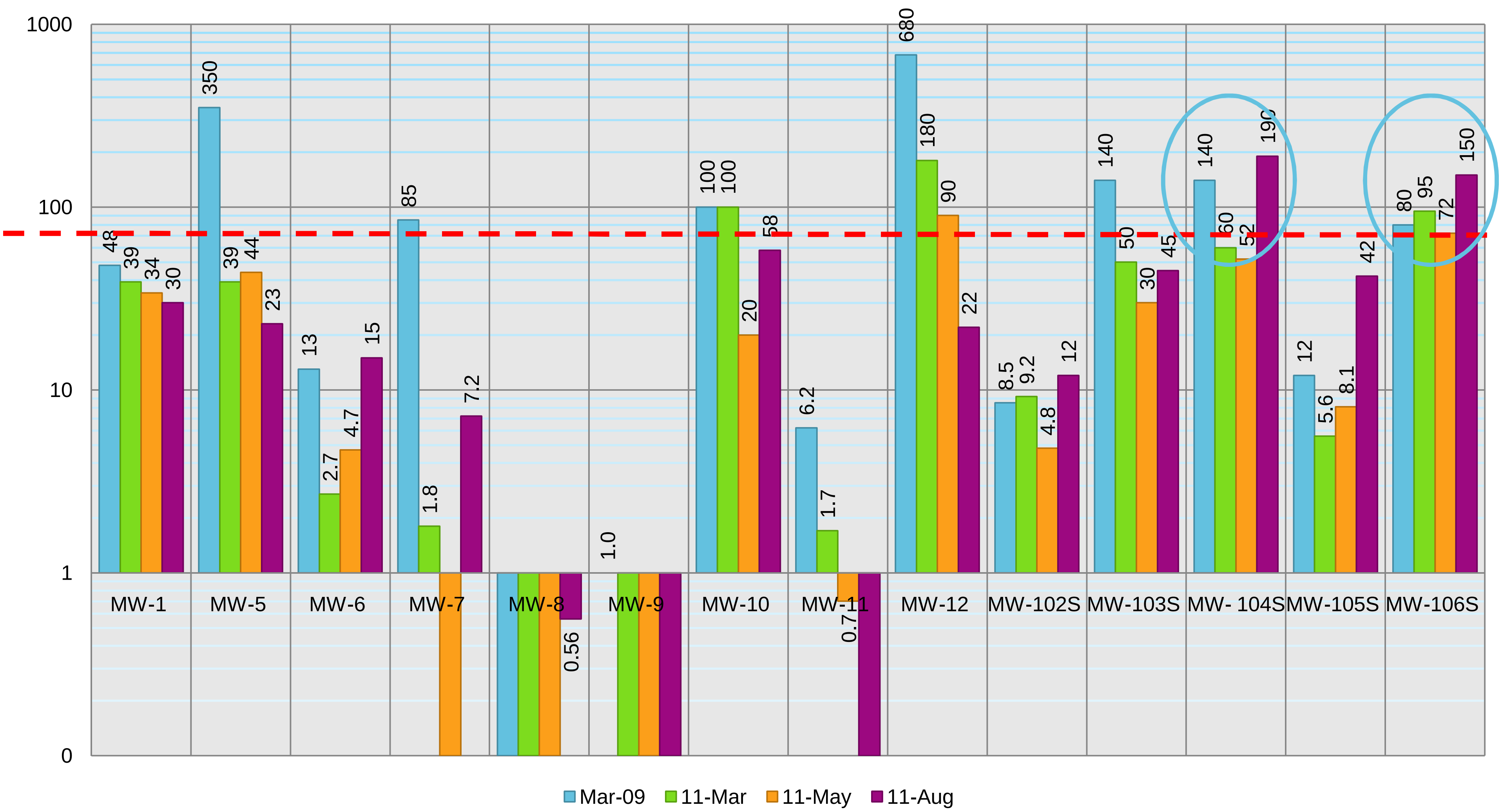
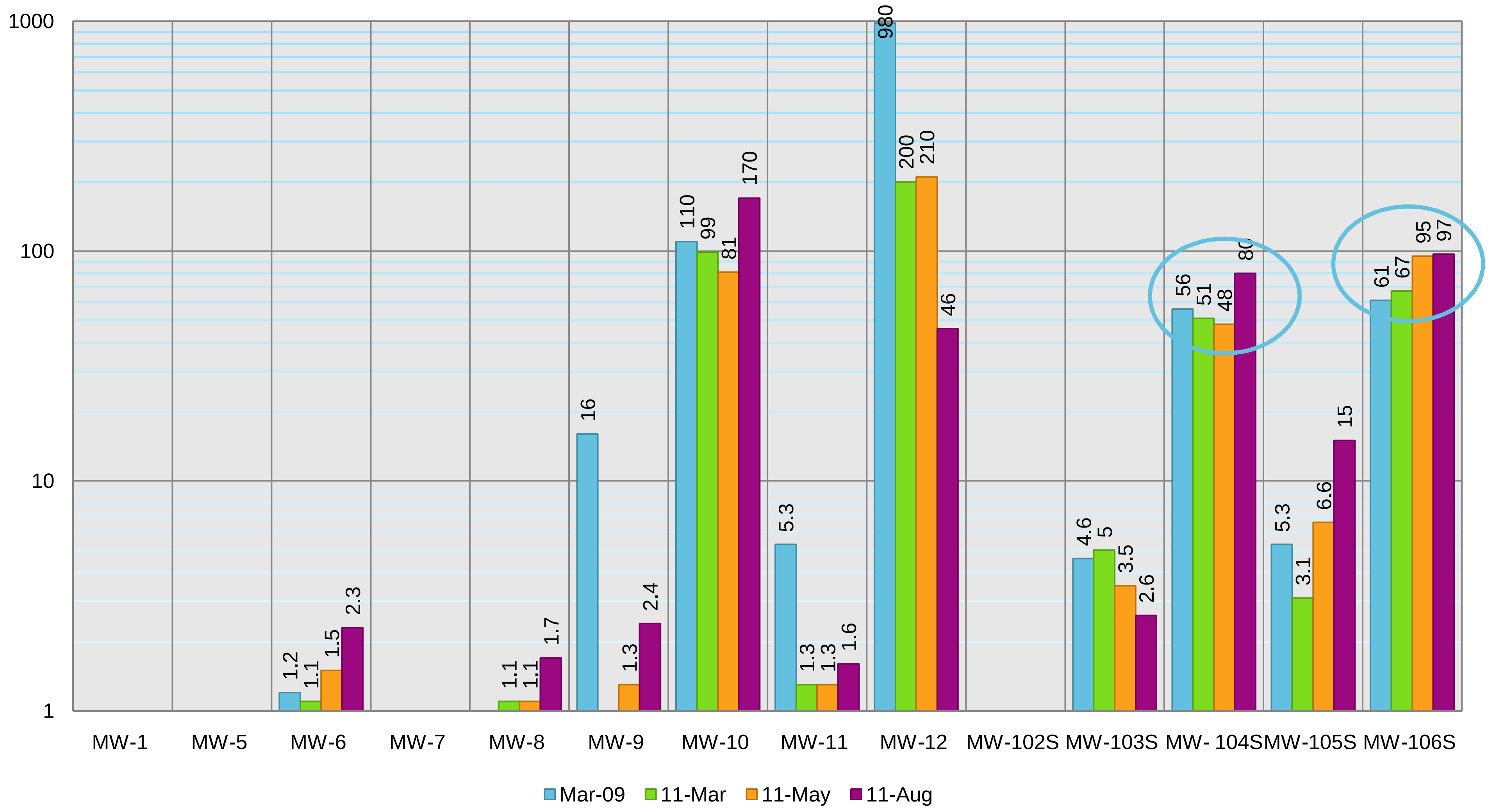
Phase II ISCO Results Summary - MTBE



Phase II ISCO Results Summary - PCE



Phase II ISCO Results Summary

2011

HOT spot wells = Significant reduction in concentrations

- MW-5, MW-10, and MW-12

TBA below GWQS in all on-site wells

- Except: MW-1, MW-5, and MW-10

MTBE below GWQS in all on-site wells

- Except: MW-10

Off Site contaminant increases

- MW-104S and MW-106S

Next Steps to Site Closure

MNA Considerations – Anaerobic

- Past system behavior suggest anaerobic conditions exist(ed)
  - PCE degradation via RD with daughter products and ~50 % reduction of COCs without active treatment over 4 yrs ('04 – '08)
- In fuel release source areas, e-acceptors (e.g., oxygen, nitrate, iron and sulfate) often absent/limited – handicapping biodegradation
- Anerobic biodegradation systems benefit from Fe-SPS once redox potential decreases again as the process supplements iron and sulfate

Life Cycle Costs: MNA with LTM vs. Additional ISCO with Re-assessment

- Given past plume stability (pre-ISCO perturbations), LTM could be in perpetuity
- One additional targeted applications of Fe-SPS equivalent to 2 years of LTM
- Additional ISCO shortens LTM time by years
  - Sequential injection events within target interval = mass reduction in zones of flux.

The End

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